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Incinerator Ash Quality, Residue Characteristics, and Control of Heavy Metal Emissions

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INCINERATOR ASH QUALITY, RESIDUE CHARACTERISTICS, AND CONTROL OF HEAVY METAL EMISSIONS

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ABSTRACT

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INCINERATOR ASH QUALITY, RESIDUE CHARACTERISTICS, AND CONTROL OF HEAVY METAL EMISSIONS

INTRODUCTION

Since 1974, the U.S. EPA has studied the practice of the incineration of hazardous waste. The early work involved performance evaluations conducted by the Cincinnati-based Industrial Environmental Research Laboratory (IERL-Ci). The later thermal destruction research program (1985 to present) was assigned primarily to the Hazardous Waste Engineering Research Laboratory (HWERL), also located in Cincinnati, with fundamental combustion research help from the Air and Energy Engineering Laboratory (AEERL) located in Research Triangle Park, North Carolina. In July, 1988 HWERL merged with the Water Engineering Research Laboratory (WERL) to form the Risk Reduction Engineering Laboratory (RREL). The responsibility for ongoing and planned research by HWERL will therefore now be assumed by RREL. (1,2)

E. Timothy Oppelt, now Acting Director of RREL, recently examined the current state of knowledge regarding hazardous waste incineration. He found that the body of knowledge concerning this field had rapidly expanded since 1980. Among Oppelt's findings are the following general conclusions about hazardous waste incinerators:

- Incineration is a demonstrated, commercially available technology for hazardous waste disposal. Considerable design experience exists and design and operating guidelines are available on the engineering aspects of these systems.

- A variety of process technologies exists for the range of hazardous wastes appropriate for thermal destruction. The most common incinerator designs incorporate one of four major combustion chamber designs: liquid injection, rotary kiln, fixed hearth, or fluidized bed. The most common air pollution control system involves combustion gas quenching followed by a venturi scrubber, a packed tower absorber, and a mist eliminator.

- Implementation of the Hazardous and Solid Waste Amendments of 1984 (HSWA) and the 1986 Superfund Amendment and Reauthorization Act (SARA), as well as industrial concerns for limiting long-term environmental liability, will encourage increasing amounts of hazardous waste to be directed to incineration facilities. While current capacity appears adequate, a near-term shortfall in commercial incineration capacity may develop. This may be particularly true for facilities which can handle hazardous waste sludges and solids.

More specific to hazardous waste incinerator ash quality, residue characteristics, and metal emissions, Oppelt identified the following:

- Limited data on incinerator ash and air pollution control device (APCD) residues suggest that organic compound levels are low and that destruction is the primary reason for high destruction and removal efficiency (DRE).

- Insufficient data are available on the fate of heavy metals in incineration systems, and the efficiency of typical air pollution control equipment to control emissions of specific metals and their salts.

- There appears to be little increased human health risk from hazardous waste incinerator emissions, based on assessments done to date. Metal emissions appear to be the most significant in the risk values which have been derived. (3)

The intent of this paper is to focus on past research, as well as ongoing and planned research, in these specific areas, namely: ash quality; residue characteristics; and metal emissions.

PAST RESEARCH

While all emissions from hazardous waste incinerators are important, the greatest interest has most often been placed on stack emissions. (3) Given the fact that ash and APCD residue are "containable" and are both labeled as and required to be managed as hazardous waste, performance measurements with respect to these incinerator waste streams were not felt to be as critical as measurements of the "uncontainable" stack emissions. Trial burn activities and past research therefore put less attention on ash and APCD residues, resulting in the limited availability of information that Oppelt found in conducting his review. However, the available information, while limited, is worth noting.

Ash/ APCD Residue

Since the inorganic components of hazardous waste are not destroyed by incineration, these materials exit the incineration system, either as bottom ash from the combustion chamber, as contaminants in scrubber waters and other APCD residues, or in small amounts in air emissions from the stack. Ash is frequently accumulated on-site in storage lagoons or in drums prior to disposal in a permitted hazardous waste land-disposal facility.

Air pollution control residues are typically aqueous streams containing entrained particulate matter, absorbed acid gases (usually HCl) and small amounts of organic contaminants. These streams are often collected in sumps or recirculation tanks where acids are neutralized with caustic and returned to the process. Eventually, a portion or all of these waters must be discharged for treatment and disposal. (3)

Combustion chamber ash and scrubber waters were analyzed for several of the incinerators tested by EPA as part of the Regulatory Impact Analysis (RIA) for the 1982 Resource Conservation and Recovery Act (RCRA) incinerator standards. (4) Recently, ten additional incinerators were also sampled to characterize ash and residues. (5)

In the RIA study, incinerator ash and scrubber waters were analyzed for organic constituents. Only two facilities had ash concentrations of organic compounds at levels greater than 35 µg/g. When organic compounds were detected, they tended to be toluene, phenol, or naphthalene at concentrations less than 10 µg/g. The same compounds were also detected in scrubber waters, usually at concentrations below 20 µg/L.

The results of the more recent ten incinerator study generally confirm the RIA results. While more organic compounds were detected across all of the facilities (19 volatile and 24 semivolatile compounds), levels in ash were typically at or well below 30 µg/g.

More compounds were detected in scrubber waters across the ten facilities than in the RIA study (nine volatiles and five semivolatiles) and in higher concentrations. Semivolatiles ranged from 0 to 100 µg/L while volatile compounds were much higher (0 to 32 mg/L).

Combustion chamber ash and scrubber water were also analyzed for metals in both the RIA study and the ten incinerator study. Detected concentrations varied widely and were a function of the amount of metal in the input waste stream at each facility and how the residues were processed. However, only three of 104 measurements of these metals in leachates from the residues and ashes exceeded allowable toxicity characteristic levels using the EPA's extraction procedure (EP) test. (3)

Overall, the data from both test programs have suggested that very small amounts of residual organic compounds remain in incinerator ash and incinerator air pollution control residues. This finding supports the contention by Oppelt that destruction and removal efficiencies reported for incinerators are almost entirely a result of destruction, rather than removal, of organic compounds.

Use of these data to project residue and ash quality for specific waste/incinerator combinations is not possible. Metal and organic concentrations are highly waste- and facility-specific. They will likely be influenced strongly by waste characteristics and by operating conditions. (3)

Metals

Metal emissions at the stack became the subject of concern in hazardous waste incineration because of the presence of metals in many hazardous wastes and because of possible adverse health effects from human exposure to emissions. Incineration will change the form of metal fractions in

waste streams, but will not destroy the metals. As a result, metals are expected to emerge from the combustion zone essentially in the same total quantity as the input. The principal environmental concern, therefore, centers around where and in what physical or chemical form the metals exit the combustion system.

Most interest on metals (such as antimony, arsenic, barium, beryllium, chromium, cadmium, lead, mercury, nickel, and zinc) has traditionally focused on stack emissions. Metals from the feed to combustion devices, when emitted in combustion gases, are typically emitted as particles rather than vapors. However, some of the more volatile elements (e.g. mercury and selenium) or their chemical compounds may be released to the atmosphere partially in the vapor state.

Most of the current state of knowledge on metal behavior in combustion has come from research on coal combustion. In general, data on metal emissions and partitioning for hazardous waste incineration are limited and often incomplete. Organic emissions have been the focus of most historical emission assessments of these facilities. Data on air pollution control device effectiveness for metals are even more scarce. (3,6-9)

The best source of metal emissions data is the previously-mentioned series of RIA incinerator tests. Average emission rates for these tests are shown in Table 1.

Wallace et al. recently reviewed all of the available metal emissions data for hazardous waste incinerators and compared them to emissions for other conventional combustion sources. The five most frequently detected metals are barium, cadmium, chromium, lead, and nickel. Mercury was not found in any of the emissions, but this was probably because only particulate metal and not vapor was sampled in the studies. The relatively volatile metals (arsenic, cadmium, lead) generally show enrichment in fine particulate emissions (i.e. higher concentration relative to their concentration on larger particles). This enrichment phenomenon is an important consideration for health assessment studies, since the fine particulates are also more likely to be inhaled.

Metal emission levels from the hazardous waste incinerators tested were equivalent to those reported for municipal solid waste incinerators. The emissions appear to be from two to 20 times higher than those from sewage sludge incinerators. (3,10)

It is difficult to extend the findings from these few tests to hazardous waste incinerators in general. Metal emissions are a function of the amount of metal input to the incinerator (which is highly variable day to day and facility to facility) as well as the efficiency of the incinerator in controlling metal emissions.

Table 1. Average Stack Emissions for Five Hazardous Waste Incinerators. [a]

Emission rate (g/kJ) and concentration on particulate (µg/g) [b,e]

Metals	Plant A	Plant B (uncontrolled)	Plant B (controlled)	Plant C	Plant D	Plant E
Sb	0.32 (8380)	0.26 (300)	c	c	f	f
As	f	c	c	c	f	d
Ba	0.052 (840)	0.19 (250)	0.11 (930)	c	0.056 (1490)	0.050 (470)
Be	f	c	c	c	f	d
Cd	0.055 (890)	0.11 (140)	0.019 (150)	c	0.012 (1120)	0.36 (4000)
Cr	0.14 (2300)	0.73 (950)	0.19 (1500)	2.5 (47500)	d	0.094 (1100)
Pb	5.4 (85500)	2.3 (3100)	0.64 (5300)	c	0.24 (25600)	9.0 (98000)
Mg	d	c	c	c	f	f
Ni	0.024 (400)	0.50 (650)	0.087 (740)	2.7 (49000)	0.052 (4570)	d
Se	f	7.0 (9200)	0.45 (3700)	c	0.29 (34600)	f
Ag	0.0008 (11.4)	c	c	0.33 (620)	0.0076 (917)	f
Ti	0.0089 (140)	c	c	c	f	f

a Adapted from Wallace et al., 1985. (10)
b Numbers in parentheses represent values for µg of metal/g of emitted particulate.
c All values below detection limit.
d Some values below detection limits, average not calculated.
e Emissions are reported as gram of particulate emitted per hour divided by the design heat release rate of the incinerator in kJ/hr.
f Information not available.

It has also been difficult to draw conclusions on APCD efficiency for metals because of the uncertainty of the sampling methods usually employed for control device input rates, the lack of particle size information and the relatively low quantities of metals available in collection samples. (3)

ONGOING/PLANNED RESEARCH

Many of the limitations noted in Oppelt's review are being addressed by ongoing and planned EPA research. Studies are being conducted both in support of regulatory development, and in response to regulations already in place.

Ash/ APCD Residue Research

It was mentioned earlier that characterization of incinerator ash and APCD residue had received limited attention. Because of the enactment of the Hazardous and Solid Waste Amendments of 1984 (HSWA), these waste streams have become the subject of recent research tests.

Among the requirements of HSWA are Congressionally-mandated restrictions which prohibit the continued land-disposal of untreated hazardous wastes beyond specified dates. The statute requires EPA to set "levels or methods of treatment, if any, which substantially diminish the toxicity of the waste or substantially reduce the likelihood of migration of hazardous constituents from the waste so that short-term and long-term threats to human health and the environment are minimized."

The listed RCRA hazardous wastes are divided into three "thirds", with dates set for promulgation of treatment regulations for each "third"; regulations for the final "third" must be set by May 8, 1990. In addition to listed RCRA wastes, the HSWA land disposal restrictions address the disposal of soil and debris from CERCLA site response actions. These CERCLA wastes will be subject to the land-ban beginning November 8, 1988.

The treatment standards are generally based on the performance of the best demonstrated available technology (BDAT) identified for hazardous constituents. EPA may establish treatment standards either as a specific technology, or as a performance level of treatment monitored by measuring the concentration level of the hazardous constituents in the waste or treatment residual or an extract of the waste or treatment residual. When possible, EPA prefers to establish treatment standards as performance levels. (11)

For a significant share of the listed RCRA F, K, U, and P wastes, incineration is a prime BDAT candidate. As such, rotary kiln incineration has been selected for BDAT tests of a number of listed wastes.

In 1987, test burns of five listed wastes [K024, K001-pentachlorophenol, K037, K086, and K087] took place at the U.S. EPA Combustion Research Facility (CRF) in Jefferson, Arkansas. The CRF houses two pilot-scale units which are used in the conduct of EPA thermal destruction research. For these particular tests, the CRF Rotary Kiln System (RKS) was used.

Sampling and analysis activities for the tests focused on the waste feed material, incinerator ash, and APCD scrubber water. Results of the analysis of ash and scrubber water for the incineration of K024 (distillation bottoms from the production of phthalic anhydride), K001-PCP (wastewater treatment sludge from wood preserving processes using pentachlorophenol), and K037 (wastewater treatment sludge from the production of the pesticide disulfoton) were recently reported by Mary Ann Curran and Ronald J. Turner, of RREL. (12)

The target list of hazardous constituents analyzed for was derived from a composite of compounds presented in 40 CFR, Part 261, Appendix VII and Appendix VIII. The list for each waste group is comprised of those compounds for which analytical methods and standards exist, exclusive of those compounds which, based on stated rationale, were unlikely to be present. (11)

Methyl ethyl ketone (MEK) and dichlorodifluoromethane were the only volatile organics detected at concentrations above practical quantitation limits in extracts of the incinerator ash. MEK, which was found in the K024, K001, and K037 ash, was detected at concentrations which were very similar to levels detected in laboratory blanks, indicating that it was most likely a laboratory contaminant. Dichlorodifluoromethane, which is also a common laboratory contaminant, was found at 11 µg/g in one of the three K001-PCP ash samples. No semivolatile constituents were detected in the ash from the three tests.

Overall, the majority of the metals in the feed partitioned to the ash. The most common metals detected in the ash were barium, copper, lead, and zinc. The individual results of metal analyses of ash from each of the three test is shown in Table 2. (13-15)

The only test in which volatile compounds were found in the scrubber water at levels above the practical quantitation limit was the incineration of K024; ethyl acetate was found in the scrubber effluent in the range of 19-36 µg/L, and in the scrubber influent at 18 µg/L. Dichlorodifluoromethane was found at 23 µg/L in one of the K024 scrubber water effluent samples.

No semivolatile compounds were detected in any of the scrubber water from the three tests.

Metals were detected in the scrubber water at low levels. The most common metals were arsenic, barium, copper, chromium, lead, and zinc. The individual results of metal analyses of scrubber water from each of the three tests are summarized in Table 3. (13-15)

Table 2. Metals Analyses for K024, K001-PCP, and K037 Ash Samples. (concentrations in µg/g)

Metal	K024	K001-PCP	K037
Ag	ND [a]	ND	ND
As	2.1-12	0.4-0.8	5-25
Ba	35-3900	21-74	130-170
Be	ND	ND	0.5-0.71
Cd	2.2	ND	2.1
Cr	20-52	1.1-8.2	80-110
Cu	21-46	2-6.8	240-940
Hg	ND	ND	ND
Ni	11-55	ND	110-180
Pb	20-1100	0.96-5.2	15-66
Sb	ND	ND	ND
Se	ND	ND	ND
Th	ND	ND	ND
V	10-64	ND	61-88
Zn	29-170	2.1-11	290-840

[a] ND = Not Detectable. The metal was not detected above the PQL (Practical Quantitation Limit).

Table 3. Metals Analyses for K024, K001-PCP, and K037 Scrubber Water Samples. (concentrations in mg/L)

Metal	K024	K001-PCP	K037
Ag	ND [a]	ND	ND
As	0.022-0.22	0.11-0.16	0.018-0.45
Ba	0.023-0.41	0.24-0.39	0.056-0.91
Be	ND	ND	ND
Cd	0.025-0.082	ND	0.05-0.16
Cr	0.036-0.65	ND	0.069-0.21
Cu	0.32-0.81	0.07-0.09	0.63-10.0
Hg	ND	0.003	ND
Ni	0.10-0.13	ND	0.10-0.12
Pb	1.4-16	0.18-0.20	1.2-11
Sb	ND	ND	ND
Se	ND	ND	ND
Th	ND	ND	0.02
V	ND	ND	ND
Zn	0.33-2.1	0.61-0.94	0.78-16

[a] ND = Not Detectable. The metal was not detected above the PQL (Practical Quantitation Limit).

Based on these results, it was concluded that rotary kiln incineration appears to be an acceptable treatment process for the three RCRA wastes. The lack of significant levels of organics (volatile or semivolatile) in the ash and scrubber water, along with the partitioning of the majority of metals to the incinerator ash are both favorable results. (12)

Metal Emissions Research

The above mentioned tests were conducted in support of existing regulations. Research tests are also being conducted and planned in support of the development of new regulations, particularly in the area of metal emissions.

While risk assessment studies conducted to date indicate that stack emissions from incinerators pose little risk to human health, metal emissions have been the dominant component of the risk levels identified. The excess cancer risk from incinerator metal emissions has been estimated to be in the range of 10^{-8} to 10^{-5} for the maximum exposed individual. (16)

Because metal emissions are controlled only indirectly by current standards through the particulate emission limit of 180 mg/standard m^3, and because the metal content of wastes which may be subjected to incineration in the future may be higher, increasing attention is being focused on metal emissions. (3)

Current regulatory thinking suggests implementation of metal emission limits and metal feed rate limits, calculated using health risk levels and dispersion modeling. Since limited information is available on metal partitioning, particle size distribution, and the metal removal capability of air pollution control devices, a conservative initial assumption of the regulations would be that metals in the waste feed exit the incinerator entirely as stack emissions. Therefore, health risk levels would be directly back-calculated to metal feed rates. As more data is collected on partitioning and APCD effectiveness, these factors would be incorporated into the calculation of the feed rate limit. (1)

Research into these areas has been recently conducted in the pilot-scale Liquid Injection System (LIS) of the U.S. EPA CRF. More extensive testing is planned for the near future in the CRF's rotary kiln.

Liquid Injection System Testing. A two part series of tests was conducted in 1987 specifically to evaluate the fate of RCRA metals fed to the LIS. The first part of the series of tests evaluated the fate of arsenic and antimony fed in a synthetic waste mixture of methanol, chlorobenzene and carbon tetrachloride. Blends of the organic compounds produced the various inlet chlorine concentrations (0 to 33.8 percent). The second part evaluated changes in the valence state of chromium, which was fed to the incinerator as trivalent chromium in a similar synthetic mixture.

The specified objectives of the tests included the following:

- Track arsenic and antimony emissions through the incinerator; study the partitioning of metals between stack vapor and particulate
- Explore the dependence of metal emissions on chlorine content of the waste feed
- Evaluate the efficiency of the packed tower scrubber
- Determine the valence state distribution of chromium in the stack (Cr (+3) vs. Cr (+6)).

During the tests, Method 5 samples were obtained before and after the packed tower (wet scrubber). Two assumptions were made in using this sampling technique. The first was that all particulate-phase metals in the exhaust gas stream were collected on the filter. The second assumption was that all vapor-phase metals from the exhaust gas were collected in the impinger; vapor-phase metals did not condense on the filter nor did they pass through the impinger. The results of the test series may be seen in Fig. 1 through Fig. 6.

Figures 1 and 2 show the effect of scrubbing on the physical state of antimony and arsenic, respectively. The figures show that, at the afterburner exit, where temperatures were above 1400 °F, the vapor phase accounted for an average of 55 percent of the collected (vapor + particulate) antimony and 35 percent of collected arsenic. At the packed tower scrubber exit, where the temperature was generally at 165 °F, the vapor phase accounted for an average of 6 percent of the collected antimony and 3 percent of the arsenic.

Figures 3 and 4 show the effect that chlorine in the feed had on the metal distribution between the vapor and particulate phases in the exhaust gases.

The average collection efficiency of the packed tower scrubber was 83 percent for antimony and 92 percent for arsenic.

Figure 5 shows the collection efficiency of the scrubber system, with and without chlorine, for chromium. Chlorine in the feed appears to have a positive effect on scrubber efficiency.

Figure 6 shows the hexavalent chromium content of the flue gas particulate and the scrubber water. The values show that between 14 and 17 percent of the chromium measured in each stream consists of the hexavalent species, with the remainder being trivalent chromium. (17)

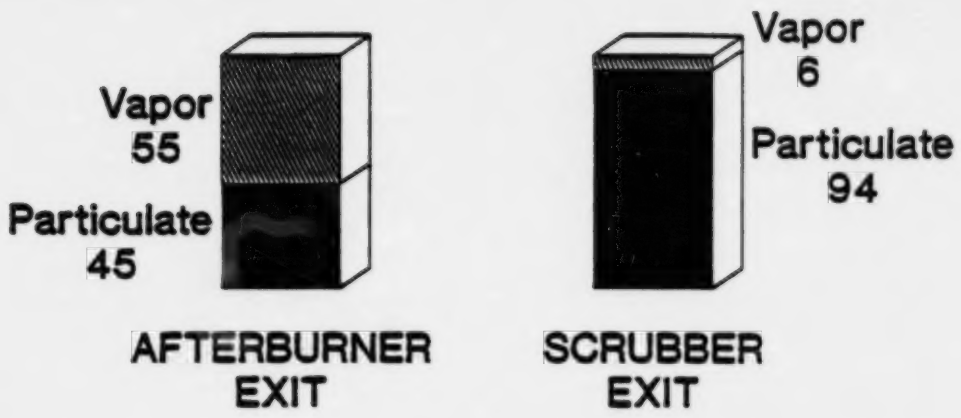

Figure 1. Effect of scrubbing on antimony distribution.

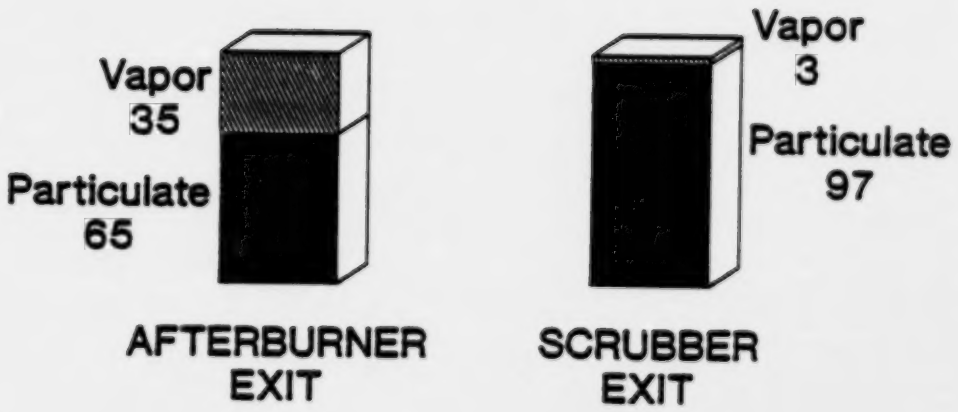

Figure 2. Effect of scrubbing on arsenic distribution.

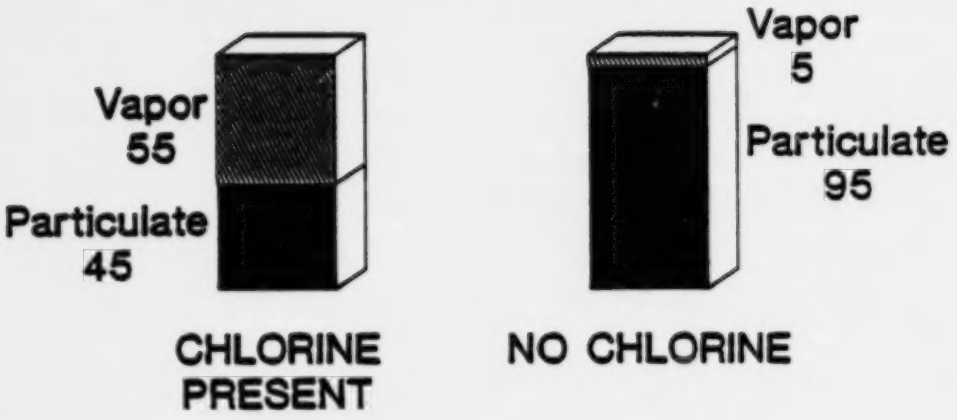

Figure 3. Effect of feed chlorine on antimony distribution at afterburner exit.

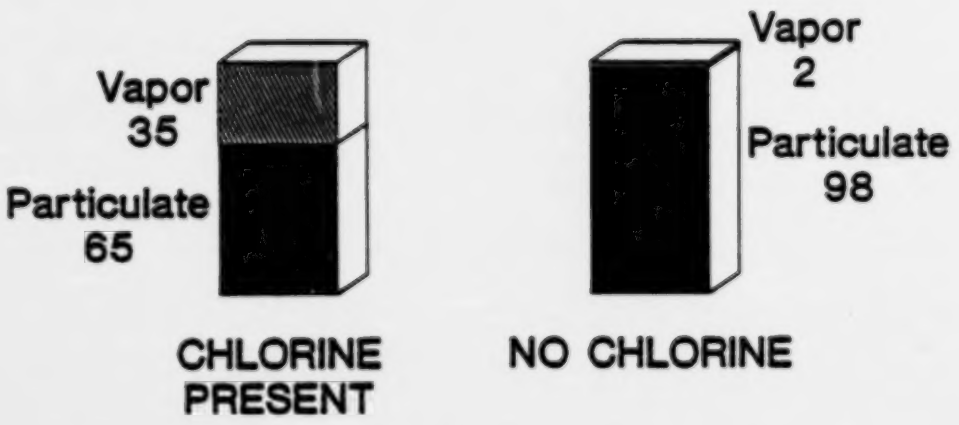

Figure 4. Effect of feed chlorine on arsenic distribution at afterburner exit.

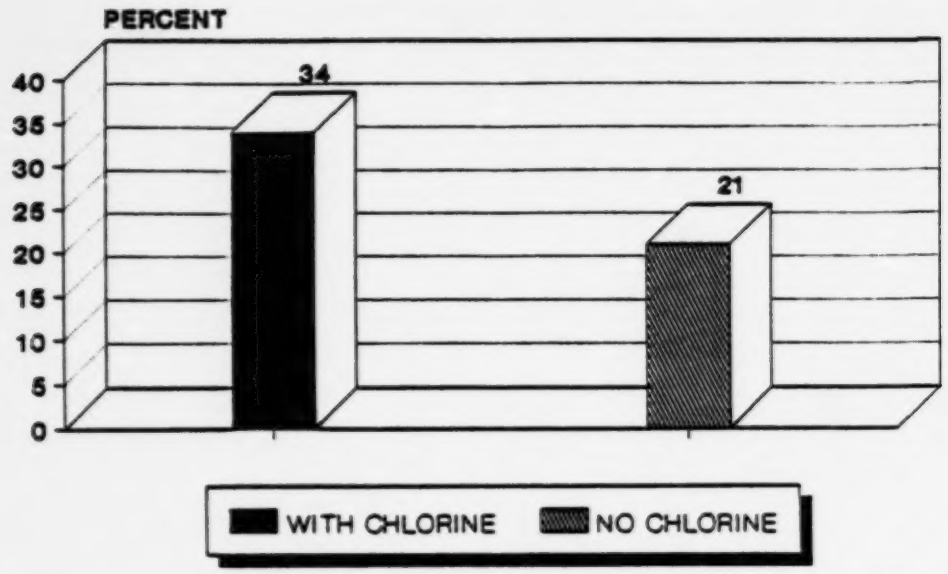

Figure 5. Effect of feed chlorine on scrubber efficiency for chromium.

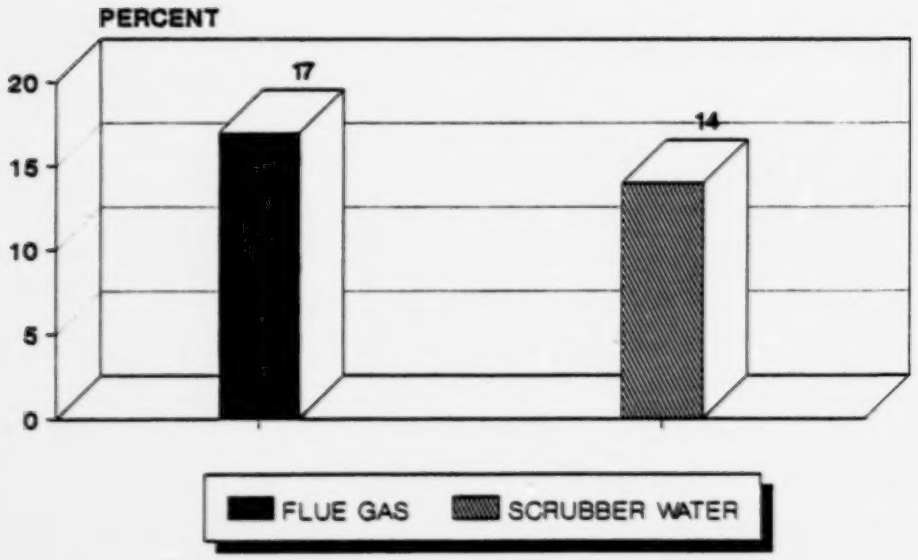

Figure 6. Hexavalent chromium as % of total measured chromium.

Rotary Kiln System Testing. To expand upon the LIS testing, three series of tests have been scheduled in the CRF rotary kiln. The first series is expected to begin in mid- to late-August. The primary concentration will be on studying the fate of Appendix VIII metals during hazardous waste incineration in a rotary kiln with venturi scrubber/ packed tower scrubber air pollution control.

A four week series of eight parametric tests will investigate the fate of arsenic, lead, cadmium, chromium, and barium. In addition, the non-hazardous constituent trace elements, copper, magnesium, bismuth and strontium will be spiked into the feed to establish whether discharge distributions of these metals may be used as indicators of hazardous constituent trace metal discharge distributions.

The synthetic waste, which will be mixed into a clay absorbent material, will be toluene-based. The composition of the waste will be varied by changing the relative amounts of toluene, chlorobenzene, and tetrachloroethylene. The parametric tests will seek to identify :

- The distribution of metal emissions among ash, scrubber water, flue gas particulate (by particle size), and vapor phase flue gas
- The sensitivity of metal fate to RKS operating conditions (rotary kiln temperature, afterburner temperature)
- The dependence of metal emissions on chlorine content of the waste feed.

An additional one-week test burn will examine the relative emissions of trivalent and hexavalent chromium. (18)

In each of the next two test series, a different air pollution control device will replace the venturi scrubber/ packed tower combination. The second series in the three will explore the effectiveness of an ionizing wet scrubber as an APCD for the control of metal emissions. The last test series will most likely investigate the combination of a spray drier and baghouse.

The information collected by these tests at the CRF should prove useful in examining the potential impact of metals upon net environmental emissions and in evaluating various regulatory strategies which may be necessary to control increased emissions.

CONCLUSION

Several areas where information was lacking were identified by Oppelt in his Critical Review. Since the time that his review was undertaken, some of the information needs have begun to be addressed. More research is being conducted on incinerator ash quality and APCD residue characterization as a result of the HSWA land disposal restrictions. Additionally, a significant amount of research on metal emissions is being conducted in support of regulatory development.

One notable difference between the information being gathered over the past few years and that from earlier years is that the more current research is being conducted in the form of designed, parametric experiments. In contrast to the earlier research, which primarily consisted of performance evaluations with many uncontrolled variables, the more recent work seeks to control variables and to determine cause and effect relationships. As such, this research should make a significant contribution to the field of incineration, and should help EPA in its overall goal of protecting human health and the environment.

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